STUDIES ON ELECTRICAL RESISTIVITY OF AN ORDERING IRON-ALUMINUM ALLOY

A THESIS

PRESENTED TO THE FACULTY OF METALLURGICAL ENGINEERING IN PARTIAL FULFILMENT OF THE REQUIREMENTS OF THE DEGREE OF MASTER OF TECHNOLOGY

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ABSTRACT

The variation of the various perturbation terms of the Coles expression of electrical resistance at a temperature is investigated in case of an iron-aluminum alloy (27.7 atomic percent Al) as a function of order. The results obtained are compared with those reported in the literature for a near stoichiometric composition alloy (24.8 atomic percent Al). The structural transition temperature of the Fe_3Al phase for the alloy under study has been determined through the study of the variation of the coefficient of thermal expansion as a function of temperature and is compared with that reported in literature.

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CHAPTER 1

INTRODUCTION

A. General:

In a perfectly periodic lattice of a metal, electrons moving in a given direction will continue to move in that direction indefinitely. A perfect lattice therefore offers no electrical resistance whatever. If, however, the lattice is not perfectly periodic, the electrons will be scattered and it is from this scattering that resistance arises.

The periodicity of the lattice may be disturbed by various factors like thermal oscillations of the atoms about their mean positions at any temperature above the absolute zero, the presence of impurity atoms with different atomic sizes and nuclear charges, the imperfections in the lattice such as vacancies, dislocations, grain boundaries etc. Electrical resistance may also arise due to eletronic factors like s - d transition in transition metals and exchange interaction of d electrons of a transition metal solute with conduction electrons of a nontransition metal solvent (1) etc.

Electrical resistance, in effect, is an additive quantity. It would be interesting to disentangle the various factors that contribute to the net observed electrical resistance at a particular temperature with a view to determine the relative roles of various factors. Such knowledge is desirable for the design and production of alloys useful in electrical appliances.

In iron-aluminum binary system in the region of 23 to 35 atomic percent aluminum an order-disorder transformation is reported.(2,3) The ordered phase is Fe_3Al and the stoichiometric composition transforms to a disordered phase at approximately 540°C. Besides the structural order-disorder transformation, a magnetic transofrmation involving the onset of ferromagnetism at Curie temperature, θ_c, occurs in this region of the phase diagram.

The portion of the equilibrium diagram as revised by McQueen and Kuczynski(2) between 20 and 30 atomic percent Al in Fe using dilatometric technique is given in Figure 1. The structural ordering temperatures and Curie points for a number of compositions in the Fe_3Al region as reported by these authors are given in Table I. A tentative equilibrium diagram based on the high temperature X-ray studies of ordering in iron-aluminum alloys as proposed by Lawley and Cahn(3) is given in Figure 2. The structural transition temperatures (T_c) of Fe_3Al determined by these authors for three alloys above the stoichiometric composition of 25 atomic percent Al are given in Table II. The ordering temperatures (ABC, Figure 2) in the Fe_3Al region reported by these authors are about 25°C higher than those reported by McQueen and Kuczynski. The present investigation on electrical resistivity studies on an ordering Fe-Al alloy refers to relatively recent and more accurate phase diagram of Lawley and Cahn(3) (Figure 2).

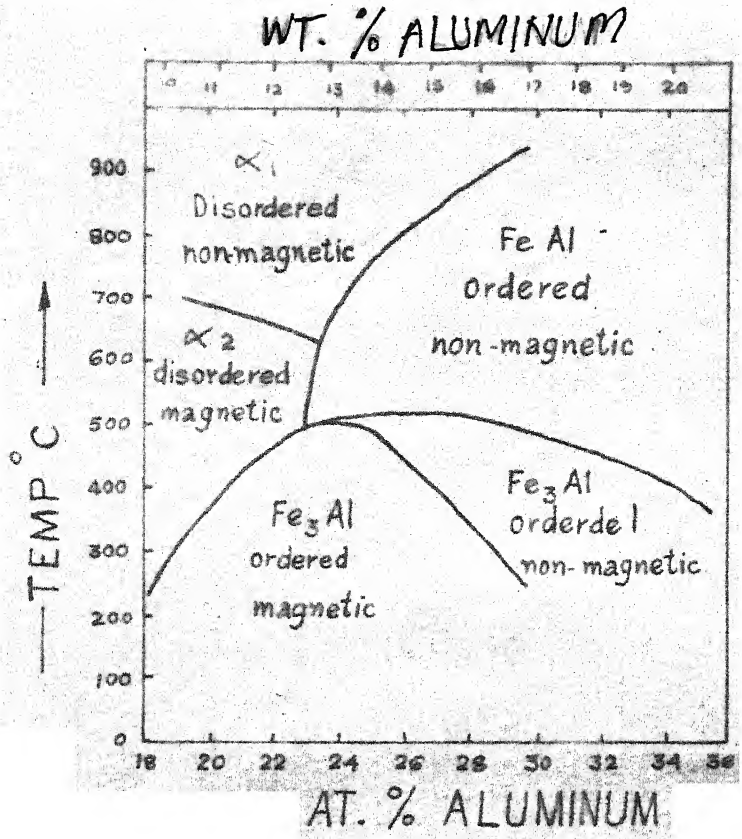


Fig. 1 (Ref. 2)

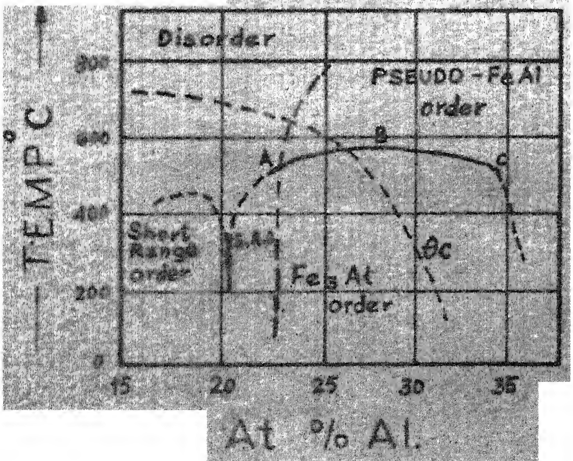


Fig. 2 (Ref. 3)

Fe-Al EQUILBRIUM DIAGRAMS

TABLE I

Composition ordering temperatures and Curie points for Fe-Al alloys. (Ref. 2)

Composition At. Pct.	Ordering Temp. of Fe_3Al °C	Ordering Temp. of FeAl °C	Curie Pt. of Fe_3Al °C	Curie Pt. of α_1 °C
19.9	360			690
21.7	460			655
22.5	475			655
23.5	500	660	500	
24.7	515	730	507	
26.0	520	840	400	
26.9	520	850	400	
29.5	490	900	270	
33.6	420			

TABLE II

Structural transition temperature Tc for disappearance of Fe_3Al order in Fe-Al alloys (Ref. 3)

At. percent Aluminum	Tc ± 3°C	Sykes and Evans C_p measurements	
		At. percent Aluminum	Tc °C
26.5	548	25.4	553, 556
27.8	550	27.6	545, 554
29.9	547	29.8	518

Any study on the contribution of various factors to the net electrical resistance at a temperature of an alloy in the Fe_3Al region of the Fe-Al system should take into account besides the structural factors, the ferromagnetic resistance component or spin disorder resistivity. According to the quantum mechanical model advanced by Mott and Stevens(4) two 3d electrons with unpaired spins are located on each atom in the body centered cubic iron. Friedel et al(5) pointed out that exchange interaction between the conduction electrons and the unpaired electrons localized on particular atoms, if sufficiently strong, might result in scattering of the conduction electrons giving rise to an appreciable term in the electrical resistance. This term is called the spin disorder resistivity or ferromagnetic resistance component. The contribution of this component decreases upon ordering of the atomic spins i.e. with the onset of ferromagnetism.

Coles(6) has given a semiquantitative equation relating the electrical resistance at a temperature of an alloy containing localized spin moments to the perturbations due to atomic disorder P_A, thermal disorder P_T and spin disorder P_S. The equation of Coles is given below:

$$\rho = F(P_A + P_S + P_T) \qquad .. \qquad (1.1)$$

The factor F in the above equation expresses the freedom of the conduction electrons and it takes into account their concentration, effective masses and density of states to which they can make transitions etc. Obviously it depends on the Brillouin zone structure. A high value of F indicates a lower degree of freedom and vice versa. Coles successfully applied the above equation to iron and its alloys.

Feeder and Cahn(7) used the Coles equation to explain the anomalous shapes of the resistance vs.temperature curves obtained for alloys in the Fe_3Al region with upto about 26 atomic percent aluminum. They concluded that the slight hump observed just below T_c for 24.8 atomic percent Al alloy (Figure 4) in this region is not due to the influence of antiphase domain boundaries as was suggested by Bennett(8) but due to the way in which F and P_A change with order. Also they successfully separated the terms F, P_A, P_T and P_S and showed their variation with order below T_c. Using the perturbation terms of the Coles equation and a temperature-corrected value of F they were able to predict quite accurately the resistances at higher temperatures of the near stoichimmetric composition alloy mentioned above.

The present investigation dealing with the study of variation of the resistivity parameters with order for an alloy of 27.7 atomic percent Al in Fe is based on the Feeder and Cahn's analysis of resistivity for the near stoichiometric alloys of the Fe-Al system. In the following section Feeder and Cahn's(7) approach of determining the influence of crystallographic order on various resistivity parameters of Coles equation and the estimation of high temperature resistivity for near stoichiometric Fe_3Al alloys is presented.

B. Influence of Crystallographic order on resistivity parameters of Coles equation:

When the state of crystallographic order changes, the lattice periodicity varies and this influences the Brillouin zone structure. Therefore with the change in the state of order besides P_A, the atomic disorder scattering perturbation term, F, the terms which expresses the freedom of conduction electrons also varies. To apply the Coles equation $\rho = F(P_A + P_T + P_S)$, therefore, it is necessary to find out how P_A and F vary with order below the critical temperature T_c. An approximate idea of this can be got by obtaining data on resistivity at and below ~~room temperature~~ of alloys quenched from different temperatures and which are consequently in different states of order. As the rate of diffusion is vanishingly small at room temperature the specimen remains in the state of order corresponding to the quenching temperature and retains corresponding values of P_A and F.

From Coles equation, one can write,

$$\rho_0^{QT} = F^{QT} . P_A^{QT} \qquad .. \qquad (1.2)$$

Here the suffix 0 indicates the residual resistivity at 0°K while the superfix QT denotes the fact that the quantities refer to an alloy quenched from temperature T. The terms P_S and P_T disappear because the zero point thermal energy and residual spin disorder are small enough to be neglected in comparison with P_A. The state of spin disorder characteristic of the quenching temperature is, of course, not frozen in by quenching.

The temperature coefficient of resistivity, $\frac{\partial \rho}{\partial T}$ at or below room temperature of an alloy quenched from temperature T is given by:

$$\left(\frac{\partial \rho}{\partial T} \right)^{QT} = F^{QT} \frac{\partial}{\partial T} (P_A + P_T + P_S) \quad .. \quad (1.3)$$

The alignment of spins is already far advanced at and below room temperature and the variation of saturation magnetization moment M_S and the spin disorder perturbation P_S with temperature is slight throughout the range of temperatures under consideration. Taylor and Jones(9) experimentally confirmed that the variation of M_S with temperature is slight below 20°C for alloys in the Fe_3Al region of the Fe-Al system. Also, $\frac{\partial P_S}{\partial T}$ is a negligibly small term for all states of order i.e. for all quenching temperatures for the alloys under consideration. Masumoto and Saito(10) and Rode(11) experimentally found that for an alloy in Fe_3Al region the saturation magnetic moment at room temperature varies by less than 10 per cent between complete order and full disorder. Therefore, we take $\frac{\partial P_S}{\partial T}$ as approximately equal to zero at or below room temperature, irrespective of the quenching temperature and even to a better approximation $\frac{\partial P_S}{\partial T}$ is small and constant for all quenching temperatures.

$\frac{\partial P_T}{\partial T}$ is also taken to be virtually independent of the state of order. The thermal perturbation P_T due to lattice vibrations is closely related to elastic properties and we can estimate how much P_T varies with order by noting to what extent an elastic modulus changes with order. Yamanoto and Taniguchi(12) showed that the change due to ordering of the intrinsic Young's modulus at room temperature is only 1 to 3 percent for alloys in the Fe_3Al region. Also the Debye temperature, which is related to the maximum frequency of oscillation of atoms at a temperature and hence directly to the thermal disorder scattering perturbation term P_T was found to be unaffected by ordering by Nemnonov et al(13). Therefore it may be concluded that the thermal perturbation is virtually independent of order and at and below room temperature $\frac{\partial P_T}{\partial T}$ can be taken as independent of quenching temperature.

The atomic disorder scattering perturbation term P_A is determined by the quenching temperature. It does not vary with temperature at and below room temperature because of low atomic diffusion rates. Therefore, $\frac{\partial P_A}{\partial T}$ is taken as equal to zero.

From the foregoing, it may be written:

$$\left(\frac{\partial \rho}{\partial T} \right)^{QT} = \alpha^{QT} \approx P^{QT} \times \left(\frac{\partial P_T}{\partial T} \right)^{QT} \approx K.P^{QT} \qquad .. \quad (1.4)$$

where K is a constant.

Relations (1.2) and (1.4) permit independent estimates to be obtained of P_A^{QT} and P^{QT} for alloys quenched from different temperatures. If the sample is quenched from a particular temperature it will retain its atomic order pertaining to that temperature. The resistance of the quenched sample can be measured at room temperature, melting point of ice and in liquid nitrogen. Since resistance and temperature have a linear relationship upto temperatures slighly above absolute zero °K, the value of ρ_0^{QT} can be obtained by extrapolating the straight line joining these points to 0°K.

The accuracy with which the ρ_0^{QT} value is determined by this sort of extrapolation was found to be quite sufficient for the present analysis by Coles, Feeder and Cahn. The temperature coefficient of resistance α^{QT} can be determined by measuring the slope of the corresponding line in the resistance vs. temperature plot. Using the data obtained as mentioned above ρ_0^{QT}, α^{QT} and ρ_0^{QT}/α^{QT} can be plotted against the quenching temperature. These three curves show respectively the variation of F^{QT}. P_A^{QT}, F^{QT} and P_A^{QT} with the state of crystallographic order in view of the equations (1.2) and (1.4).

With the help of the parameters F^{QT} and P_A^{QT} determined as mentioned above an attempt can be made to interpret the experimentally determined resistance vs. temperature curve and to find the course of variation of P_S with temperature. At a particular temperature T, the resistance is expressed by:

$$\rho^T = F'^T(P_A^T + P_T^T + P_S^T) \qquad \text{--} \qquad (1.5)$$

Here the superfix T represents the value of the corresponding term at temperature T. P_A^T is the atomic disorder scattering perturbation term and is purely configurational. P_T^T stands for the thermal vibration scattering perturbation term. It depends upon the mean square displacement of the vibrating atoms and at and near Debye temperature $\frac{\partial P_T}{\partial T}$ remains constant as shown by Mott and Jones(14a). Therefore, $\frac{\partial P_T}{\partial T}$ is taken as independent of temperature above 100° C, for the present study.

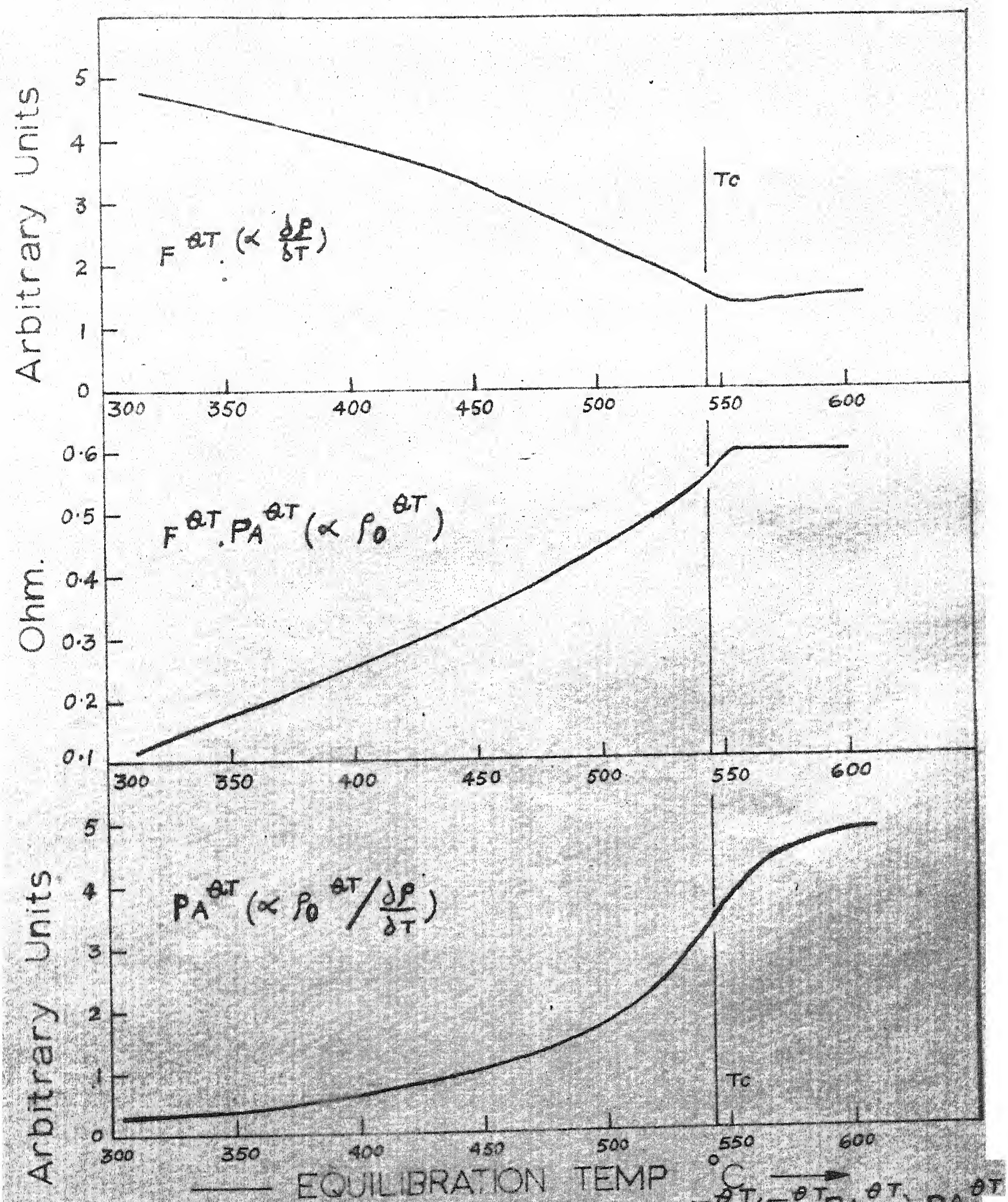
The spin disorder scattering potential P_S^T will be left aside for the moment.

The meaning of the dash in F'^T is explained below. The electron freedom F^{QT} as introduced before cannot be used in equation (1.5). This is so because even for a fixed configuration of the alloy F must decrease with rise of temperature as a consequence of the quantum theory of electrical resistance of transition metals (14b). In these metals much of the resistance arises from the s-d and p-d scattering transitions. The transition probability and the factor F, therefore, depends on the number of energy states in the d band within an energy range of K T at the Fermi surface. When the d band is nearly full, the density of states N(E) is a steeply falling function of E and therefore the number of available states does not increase proportionately to T. The resistance of a pure transition metal therefore does not rise proportionately to T.

In terms of the present formalism, this implies for iron and its alloys the freedom factor F falls with rising temperature. The symbol F will be reserved for the configurationally determined value, determined from measurements at 20°C, 0°C and -196°C of a quenched alloy. The true value, at any higher temperature will be F' and is lower than F for the same state of order. Another factor contributing to the lower value of F at higher temperature for the same state of order is the spin disorder becoming predominent after a particular temperature θ_c. Above the temperature θ_c the freedom of the conduction electrons is reduced due to spin disorder scattering too. Hence in the region of interest to us F will have a lower value than that configurationally determined and we term it F'. We do not know the variation of F and F' with temperature. We only know that F' is less than F. Omitting the spin disorder term and taking the value of F^{QT} without temperature correction, the value of the resistance at any temperature is given by

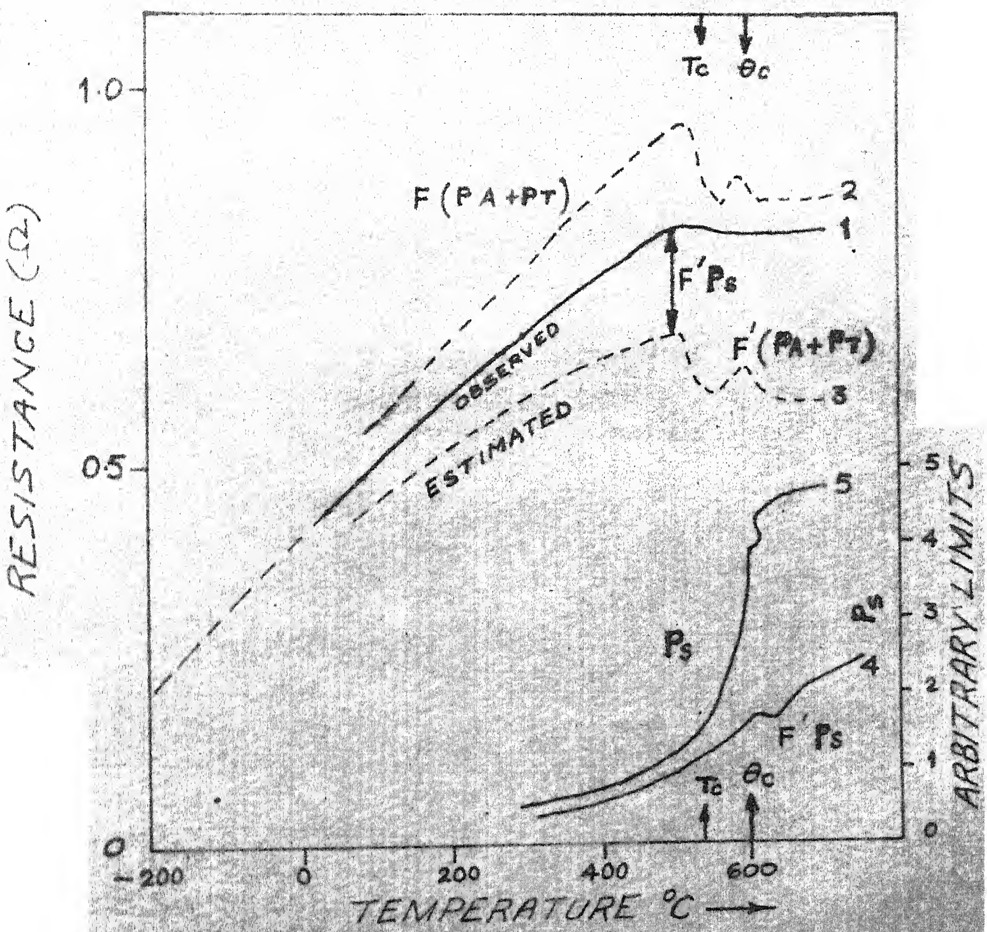
$$\rho^T = F \ (P_A + P_T) \qquad .. \qquad (1.6)$$

The value of ρ^T in the euqation (1.6) can be obtained by extrapolating each line in the plot relating the resistance at 0°K, -196°K, 273°K, for each quench temperature to the corresponding temperature T. This simple extrapolation procedure is justified since $F^{QT} = F$ exhypothesi, is independent of temperature for a given state of order i.e.



RESISTIVITY PARAMETERS $F^{\theta T}$,($F^{\theta T}$.$PA^{\theta T}$),$PA^{\theta T}$ As Function of Quenching Temp for 24·8 at % Aluminum Alloy (Ref.)

Fig 3



Observed and computed high temperature resistivity values for 24.8 AT % Aluminium alloy (Ref. [illegible])

Fig. 4.

quenching temperature and $\frac{\partial P_T}{\partial T}$ which together with F^{QT} determines the slope of the lines in the above mentioned figure is also approximately independent of temperature.

Since F' is less than F and for a temperature T it is not known to what extent F' is less than F one can take arbitrarily in the temperature region 300 to 600°C (F - F') varies proportionately to absolute temperature and F'/F = 2/3 at 600°C. Using the corrected value of F equation (1.6) can be rewritten as

$$\rho^T = F' (P_A + P_T) \qquad .. \qquad (1.7)$$

The experimentally determined value of the resistance at a temperature corresponds to the ρ^T value in equation (1.5) while ρ^T in equation (1.7) corresponds to the estimated value. The difference between these two values of ρ^T, obviously, is equal to F' P_S. Therefore, variation of P_S with temperature (hence, order) can be known if F' at each temperature is known. Infact, F' value must be known for evaluating ρ^T value from equation (1.7). The procedure for evaluating F' is given below:

Based on the assumption of Feeder and Cahn, one can write for any temperature T°K in the region 573-873°K,

$$(F - F') = AT \qquad .. \qquad (1.8)$$

Where F and F' have their usual meaning and A is a constant. The value of A can be calculated if F'/F value at any temperature is known. This has arbitrarily been assumed to be 2/3 at 600°C for the stoichiometric alloys of Feeder and Cahn. For the alloy in the present investigation, this value is taken as 2/3 at 590°C. The arbitrariness involved in giving a value to this ratio does not affect the study of the variation of P_S with temperature, though it might affect the accuracy with which the high temperature resistivity could be estimated. In equation (1.8) F value can be substituted from equation (1.4). The constant A can then be evaluated for the temperature for which F'/F value was arbitrarily taken as 2/3. Once the constant A is determined F' for any temperature T in the region 300 - 600°C can be determined since F is known through equation (1.4).

Now the variation of P_S with temperature can be determined since $F'P_S$ and F' are known for a number of temperatures in the region of interest.

Feeder and Cahns data based on the above analysis for the variation of the resistivity parameters of Coles equation with order for 24.8 atomic percent Al alloy are summarised in Figure 3 and 4. Figure 3 gives the variation of F^{QT}, P_A^{QT} and ρ_0^{QT} with order while Figure 4 shows the observed and estimated resistance values at high temperatures. Also in Figure 4 the variation of $F'P_S$ with temperature are shown as an insert.

CHAPTER 2

STATEMENT OF THE PROBLEM

Feeder and Cahn(7) have made a detailed study of the resistivity parameters of Coles equation as function of crystallographic order for the near stoichiometric alloys in the Fe_3Al region of the Fe-Al system. They were able to estimate quite accurately the high temperature resistivities of these alloys using these parameters.

No work on determination of resistivity parameters of Coles equation as a function of order appears to have been done on other compositions in this region of the phase diagram. The present investigation aims at studying the variation of these parameters as a function of crystallographic order essentially on the lines followed by Coles and Feeder and Cahn for an alloy of approximately 28 atomic percent aluminum. This composition is selected because it has the interesting feature of having the ferromagnetic Curie temperature θ_c($\sim$430°C) below the structural transition temperature T_c unlike those near the stoichiometric composition of Fe_3Al. It can be observed in Figure 2 that for alloys with below 25 atomic percent aluminum T_c is less than θ_c. Between T_c and θ_c two opposing factors influence the resistance in this alloy. They are the atomic order persisting upto T_c and the spin disorder scattering predominant above θ_c. It will be interesting to study the variation of Coles resistivity parameters with order in such an alloy.

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Lawley and Cahn(3) report that near the composition of 28 atomic percent aluminum complete order can be obtained on proper heat treatment contrary to the expectation that this should be possible for stoichiometric composition alloy. The results of Feeder and Cahn(7) also indicate that perfect order cannot be achieved in the alloys with stoichiometric composition. Lawley and Cahn(3) observe that maximum critical temperature occurs at approximately 28 atomic percent aluminum. These authors explain the shift in the maximum order and the ordering temperature from the stoichiometric composition as due to a magnetic component in the ordering 'force' in conjunction with a Curie temperature that varies rapidly with composition. This sort of displacement is reported in Nickel-Iron system near the composition Ni_3Fe by Lyashchenco et al(15,16) and the above explanation was first proposed for this system. The study of the variation of Coles resistivity parameters with order and resistance vs.temperature data reported in this investigation might be useful for studies on order-disorder transformation of fully ordering Fe_3Al alloy.

The present investigation aims at conducting the dilatometric studies on the alloy under consideration with a view to check the structural transition temperature of the Fe_3Al phase of the alloy under investigation and compare it with that from other sources.

CHAPTER 3

EXPERIMENTAL DETAILS

A. Alloy Preparation: Alumino Thermic Process:

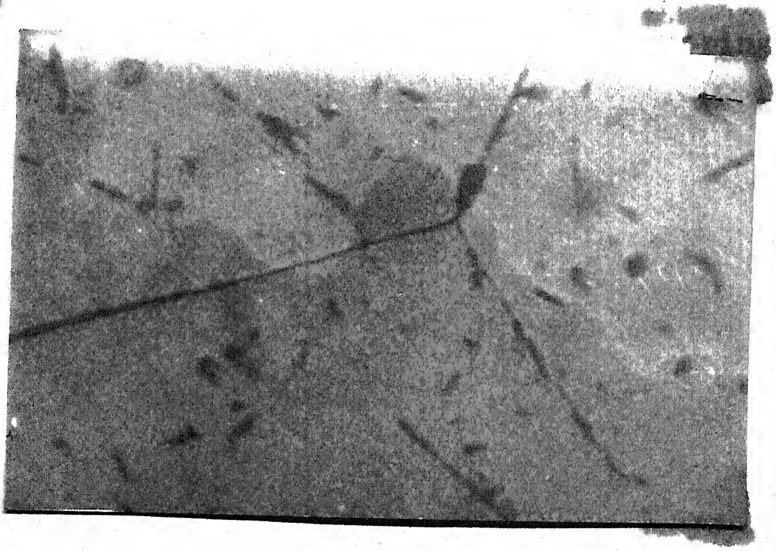
The alumino-thermic technique consists of production of ferro-alloys from the metallic oxides through reduction of these oxides by aluminum powder(17). This is a highly exothermic reaction and the heat of the reaction is sufficient for keeping the metal in molten state. Often the temperature of the melt rises to 2500°C. The metallic oxides and aluminum used in the process are in powdered state (approximately -32 mesh). On ignition of the reaction mass, the aluminum combines with the oxygen content of the metallic oxides yielding a slag consisting mostly of aluminum oxide and a metallic regulus. The reaction is completed within a few seconds of the ignition and the melt is ready for tapping within a minute.

For the production of Fe-Al alloy, mill scale powder of composition FeO-20.84 per cent and Fe_2O_3 - 78.36 per cent and aluminum of 99.77 per cent purity were used. The aluminum used has iron as a major impurity approximating to 0.22 per cent. The reactions that occur on ignition are:

$$2\ FeO + 4/3\ Al = 2Fe + 2/3\ Al_2O_3 + 137{,}670\ cal.$$

$$2/3\ Fe_2O_3 + 4/3\ Al = 4/3\ Fe + 2/3\ Al_2O_3 + 137{,}500\ cal.$$

For a charge consisting of 5 Kg. of mill scale, to produce an alloy with approximately 28 atomic percent aluminum,



X 100

Photomicrograph of the as cast sample of 27.7 atomic percent aluminum alloy used in the present investigation.

Figure 5

the aluminum powder required, for reduction, theoretically is 2.2656 Kg. However 2.3 Kg. of aluminum powder was used, the extra being to compensate for losses due to evaporation at high temperature and into the slag. The mill scale and alumnium powders in the calculated proportion are thoroughly mixed and charged into a well baked magnesite crucible which served as a reaction vessel. The ignition of the ~~mixture~~ was done with a magnesium match stick. The reaction took approximately 30 seconds for completion. The metal was tapped into a cylindrical sand mold with a diameter of 2" and length of 6". The tapping was completed within 2 minutes of the ignition of the mixture. Iron in the sample was estimated to be at 72.3 atomic percent by chemical analysis and aluminum in the alloy is calculated to be 27.7 atomic percent by difference. As cast the alloy was quite hard (average Rc 35) and brittle. The grains were quite big and can be seen with the naked eye. Micrograph of the as cast sample at a magnification of X100 is shown in Figure 5. Big grains with inclusion of Al_2O_3 can be seen in these micrographs. Al_2O_3 is an insulator and does not exhibit any phase transformations in the range of temperatures of our interest. Also, we are interested in relative resistance values expressed in ohms and as such the presence of Al_2O_3 inclusions are not detrimental to our studies.

B. Test Specimen Preparation:

As the alloy is hard and brittle with coarse grain size, the usual shaping operation involving cold and hot working are found inapplicable. Sykes and Bampfylde(18) were unable to work, either hot or cold, the alloys containing more than 16 weight percent aluminum. Alloys with aluminum content lower than 16 percent by weight are classified into two groups containing 0-5 percent and 5-16 percent aluminum, respectively(19). Alloys in the first group can be either hot worked or cold worked without any difficulty; alloys in the second group are too brittle for cold work but can be hot worked. This can best be performed in a narrow temperature range, the optimum forging temperature increases with increasing aluminum content to 1250°C for a 16 wt percent alloy. At the correct temperature, alloys will withstand quite heavy reductions and can be rolled to 22- gauge sheets or to 1/8-in-diam. wire. For alloys in the first group wire drawing practice does not present much difficulties. In the second group too, upto 14 wt. percent aluminum wire can be drawn at elevated temperatures, the temperatures being below the recrystallization temperature. With higher aluminum contents in the alloys wire drawing is extremely difficult.

The alloy under study belongs to the second group with an aluminum content of 15.4 percent by weight, (27.7 atomic percent). Wire drawing of this alloys is not feasible due to high aluminum content. For electrical resistivity measurements the specimen could be ideally either in a wire form or narrow strip shape.

For making the strip out of the cast sample, hot forging at 1250°C with controlled blows to bring the casting to shape was attempted. Good reductions in size were obtained, but oxidation at the boundaries of the elongated grains was considerable. Hence the sample prepared by hot working could not be used for the present studies on electrical resistivity.

The specimen about 1" long and 1/8" thick and 1/8" wide was made by cutting the casting into strips of about 1/4" to 1/8" on a surface grinder. The specimen so prepared does not exhibit any oxidation at grain boundaries and is strong enough to withstand the heat treatments given to it.

C. Heat Treatment:

The sample has been vacuum-sealed in a quartz tube and annealed at 800°C for 5 hours and quenched in silicone oil. This treatment removes the effect of previous cold work$^{(7)}$.

To find the variation of P, P_A and ρ_0 the residual resistivity, with order, we had to retain the corresponding high temperature order at room temperature and measure the resistance at room temperature, 0°C and -196°C. The sample is drop quenched from 610°C, after retaining it at this temperature for approximately 2 minutes, into saturated salt solution. The salt solution is used because it helps in retaining the high temperature order very effectively.$^{(7)}$ As the sample is small and the temperature in the Kanthol-wound well-insulated furnace is maintained constant, the sample will have the same order throughout its volume. In case of near stoichiometric composition alloys the time required to equilibrate the samples is of the order of few seconds above T_c temperature and below this temperature of the order of 1 hour at 400°C and 18 hours at 330°C $^{(20,2)}$. The equilibration times for the alloy under study are given in column 1 of Table IV and these are approximately fixed after studying the resistance at a temperature vs. time curves for various Fe_3Al alloys$^{(20,2)}$. These equilibration times in case of alloy under investigation are sufficiently higher than those at which one would normally expect the alloy to become equilibrated. After quenching from 610°C, the resistance of the sample is immediately measured at room temperature, in ice and in liquid nitrogen. The sample is then heat-treated at 590°C and the same operations are repeated. The equilibration of the sample is carried out in steps of 20°C till 330°C. After each equilibration step, the operations of quenching, measurement of resistance at room temperature, in ice and in liquid nitrogen are performed.

For measuring the resistivity at various temperatures the sample is taken into the disordered state at 610°C and is cooled slowly at the rate of 1-2°C per min. using an 'Electronik' program controller. This rate of cooling is reported to be sufficient to maintain the sample in the state of order at the corresponding temperature$^{(7)}$.

Iron-aluminum alloys are resistant to oxidation at moderate temperatures. The resistance to oxidation increases with increase in percentage of aluminum. For the near stoichiometric composition alloy, with which Feeder and Cahn worked the oxidation at 600°C was negligible(7). So with the alloy under study now, resistivity measurements were made at about the same temperature in air itself. The maximum temperature reached was 590°C. There was no visible mark of oxidation after cooling from this temperature.

D. Resistivity Measurements:

On each end of the sample two pure iron lead wires were spot welded. The end two wires are used as current carriers while the middle two are used as potential leads for measurements of resistivity with a Kelvin Double Bridge. The Kelvin Bridge could measure resistance between the two potential leads accurately upto the 4th decimal place. The special advantage of using a Kelvin Bridge in the present studies is that it does not take into account the resistance offered by the lead wires and contacts and measures only the resistance of the length of the sample between the potential leads. All the resistivity measurements reported in this investigation are made using the Kelvin Double Bridge.

E. Dilatometric Studies:

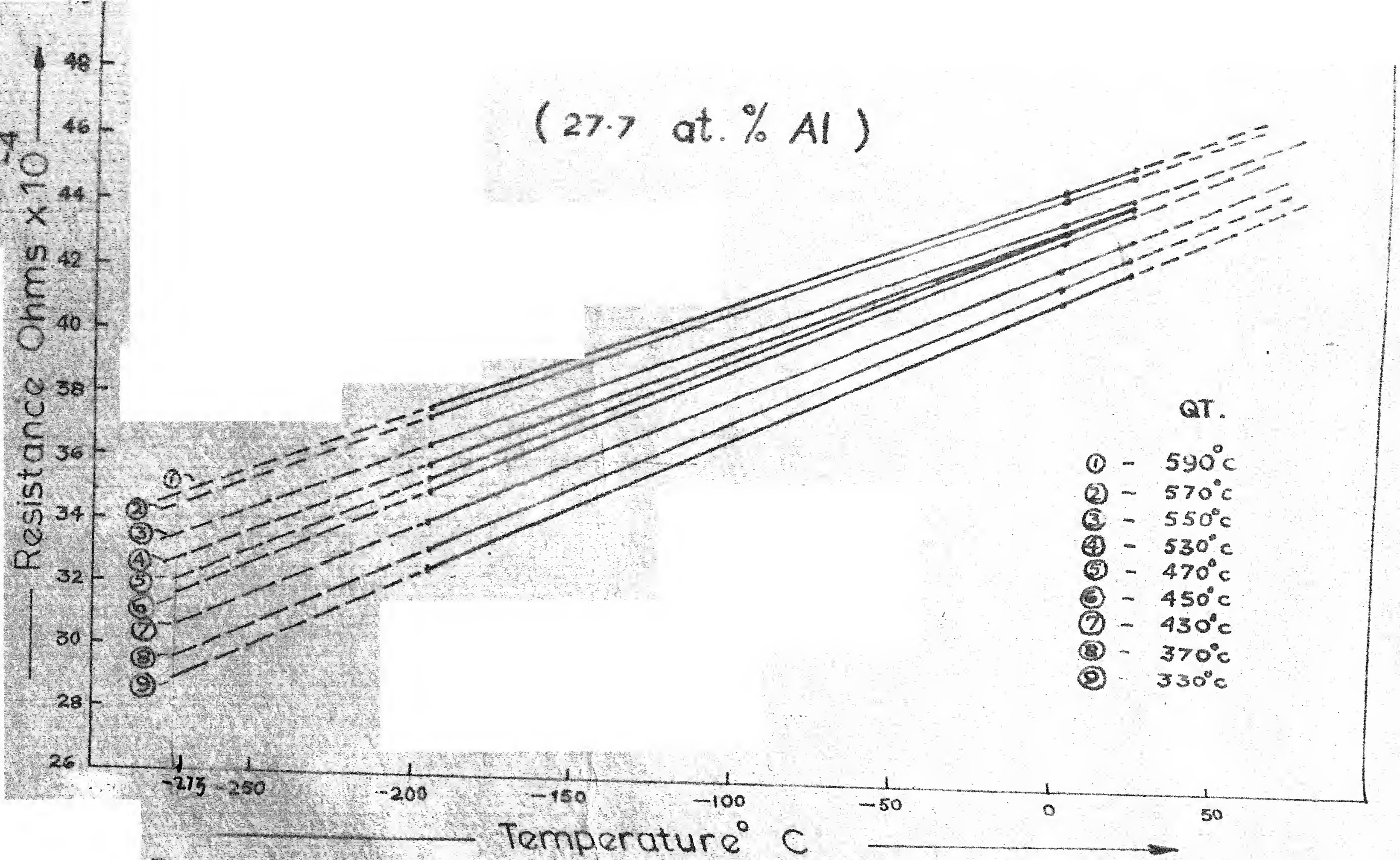
The expansion of the sample with increasing temperature was measured with the Linear voltage differential transformer (LVDT) supplied by the Daytronic Company. This instrument measures accurately the expansions of the order of 0.00002". The output in millivolts from the LVDT is fed to the Y axis of a X-Y recorder. Temperature of the sample (in MV) as measured by a chromel-alumel thermocouple is fed to the X axis of the recorder. The sample (1" long, 1/4" dia.), originally in ordered state was heated in a well insulated furnace at the rate of 1° to 1.25°C per minute. This slow heating rate was obtained using 'electronik' temperature controller supplied by the Honeywell Company. Quartz tube about 10" long and closed at both ends usually used to transfer the elongations of the sample to the dial gauge in the conventional dilatometric experiment, was used in the present study also. At the top of the quartz tube the transducer of the LVDT was fixed. The co-efficient of thermal expansion was calculated from the data obtained from the X-Y recorder.

CHAPTER 4

RESULTS

The specimen of 27.7 atomic percent Al alloy prepared as described in the previous chapter was disordered at 590°C. Resistance values measured as a function of temperature as it is cooled at the rate of 1-2°C per minute, are given in Table III and Figure 8 (Curve 1). The experimental data of the present investigation are given in Table IV. Column 1 of this table gives the quenching temperature while columns 2 to 4 give the resistivity values corresponding to this quench temperature as measured at 20°C, 0°C and -196°C respectively. From these data Figure 6 is drawn. The slopes of the lines in Figure 6 give $\frac{\partial \rho}{\partial T}$ and we know F^{QT} is proportional to this as already mentioned in Chapter 1, B. Extrapolation of the lines in Figure 6 to 0°K gives the ρ_0^{QT} values corresponding to the quench temperatures T while extrapolation to T itself gives the value of ρ^T ($= F\,(P_A + P_T)$) of equation (1.6). The slopes of the lines in Figure 6 and the extrapolated resistance values ρ_0^{QT} and ρ^T are given in columns 5, 6 and 8 and these respectively correspond to F^{QT}, $F^{QT}.P_A^{QT}$ and ρ^T (of equation 1.6). In column 7, P_A^{QT} value ($\propto \rho_0^{QT}/\partial\rho/\partial T$) is given.

The value of the constant A of equation (1.8) assuming F'/F arbitrarily as 2/3 at T = 863°K is calculated to be 0.1448×10^{-8} in case of the alloy under investigation. The (AXT) product is calculated, this being equal to the difference between F and F' values and is given in column 9. F' can be calculated knowing F



Resistance Values at Low Temperatures of Quenched Sample

Fig. 6.

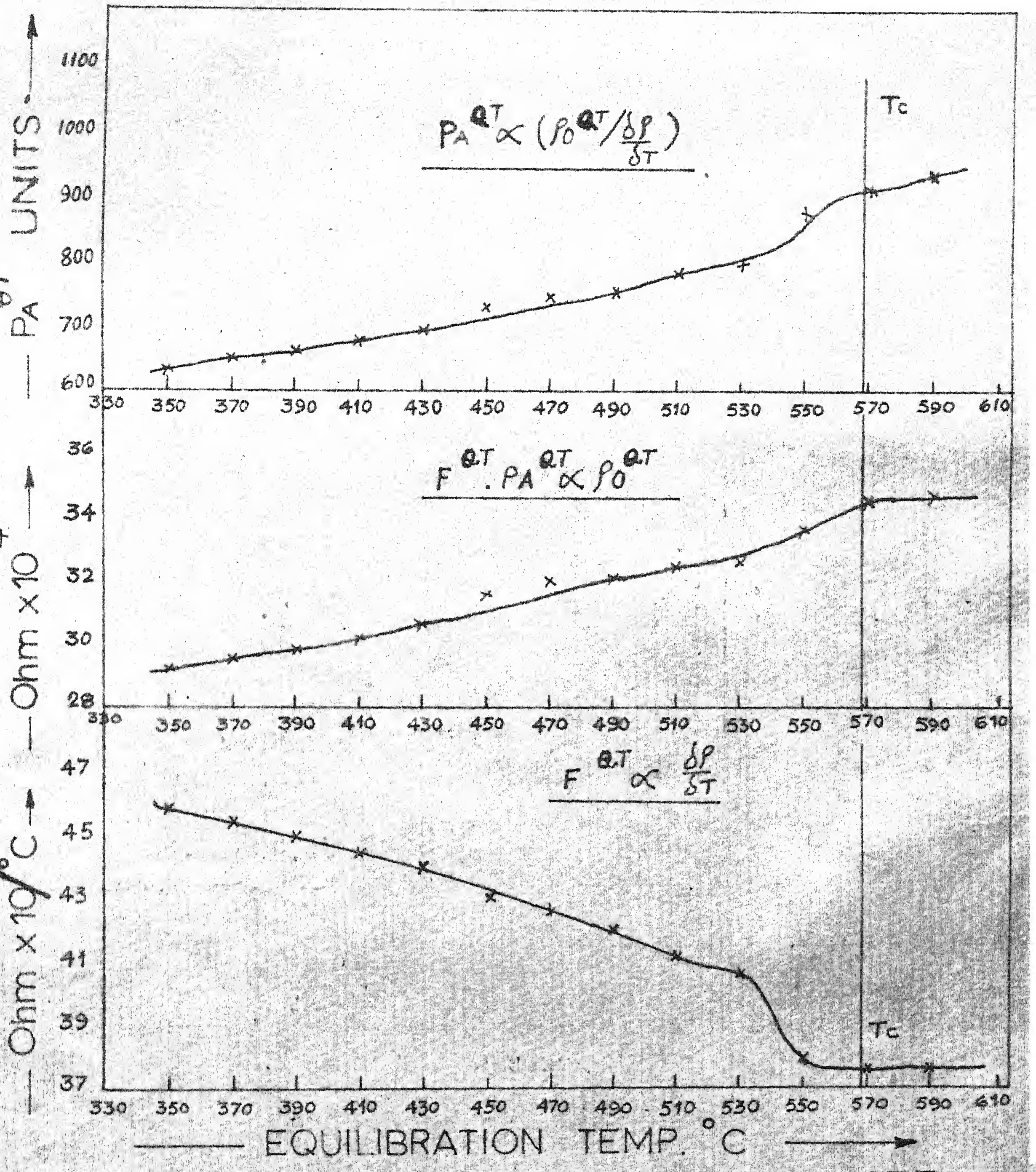
TABLE III

Resistance values at various temperatures for 27.7 atomic percent Al alloy of present investigation

Temperature °C	Resistance ohm x 10^{-4}	Temperature °C	Resistance ohm x 10^{-4}	Temperature °C	Resistance ohm x 10^{-4}
30	41.0	220	48.1	410	55.4
40	41.3	230	48.5	420	55.7
50	41.7	240	48.9	430	56.1
60	42.1	250	49.3	440	56.5
70	42.5	260	49.6	450	56.8
80	42.8	270	50.0	460	57.2
90	43.2	280	50.4	470	57.6
100	43.6	290	50.8	480	58.0
110	44.0	300	51.2	490	58.4
120	44.3	310	51.5	500	58.8
130	44.7	320	51.9	510	59.2
140	45.1	330	52.3	520	59.2
150	45.5	340	52.7	530	59.2
160	45.8	350	53.0	540	59.2
170	46.1	360	53.4	550	59.2
180	46.6	370	53.8	560	59.2
190	47.0	380	54.2	570	59.2
200	47.4	390	54.6	580	59.2
210	47.7	400	55.0	590	59.2
				600	59.2

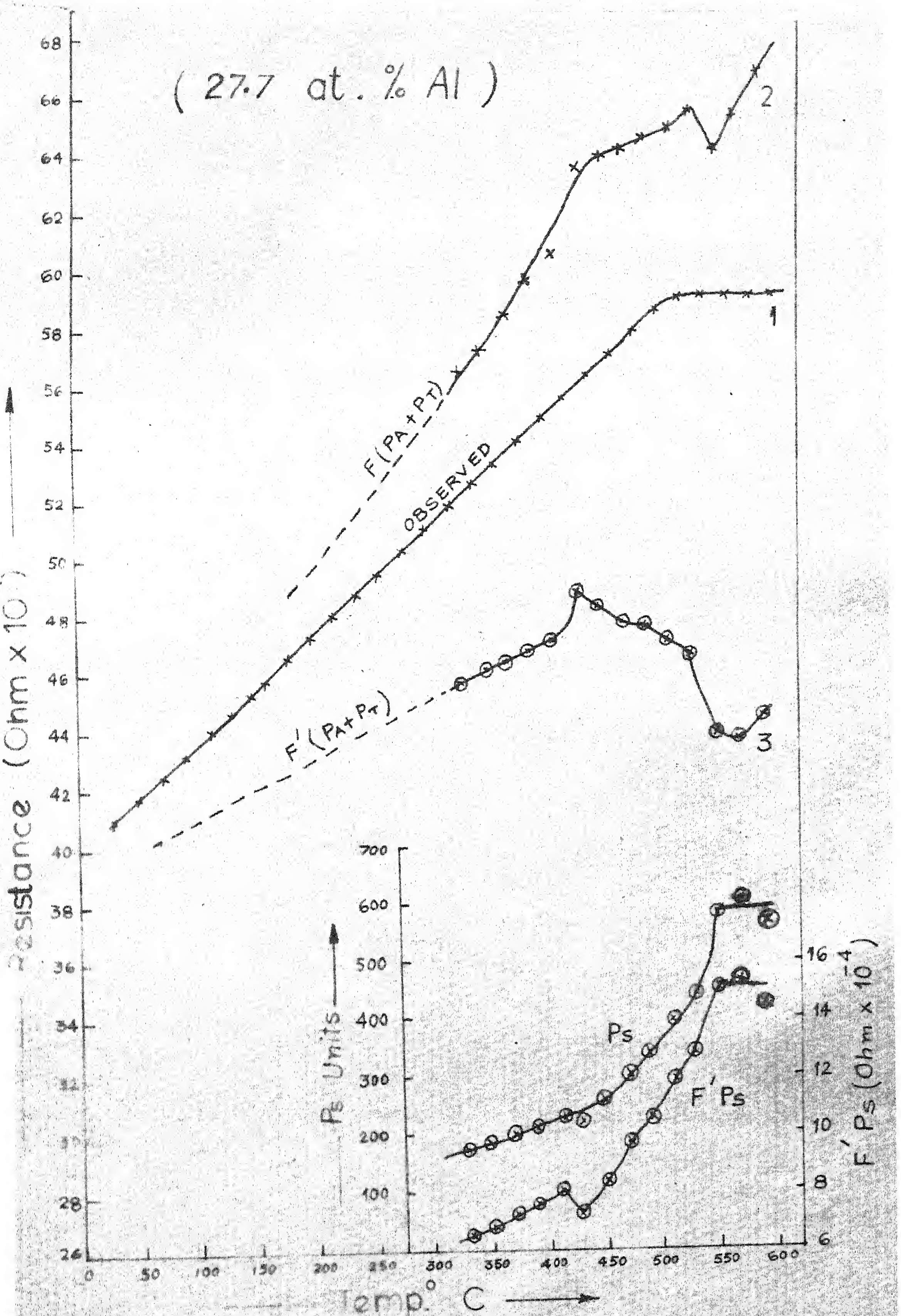
TABLE IV – EXPERIMENTAL DATA OF THE PRESENT INVESTIGATION

1		2	3	4	5	6	7	8	9	10	11	12	13	14	15
QUENCHING TEMP. °C & TIME, MTS.		RESISTANCE, OHM $\times 10^{-4}$ AT			$F^{\alpha T}$ $(\propto \partial\rho/\partial T)$ OHM $\times 10^{-5}/°C$	$F^{\alpha T} \cdot \rho_A^{\alpha T}$ $(\propto \rho_0^{\alpha T})$ OHM $\times 10^{-4}$	$\rho_A^{\alpha T}$ $(\propto \rho_0^{\alpha T}/\partial\rho/\partial T)$	ρT $(=F(\rho_A+\rho_T))$ OHM $\times 10^{-4}$	$A \times T$ $(=F-F')$ $\times 10^{-5}$	F' $\times 10^{-5}$	F'/F	ρT $(=F'(\rho_A+\rho_T))$ OHM $\times 10^{-4}$	ρT $(=F'(\rho_A+\rho_T+\rho_S))$ OBSERVED OHM $\times 10^{-4}$	$F' \cdot P_S$	P_S
TEMP	TIME	20°C	0°C	−196°C											
590	5	45.7	45.0	37.6	.375	34.7	946.9	67.0	.125	.25	.666	44.6	59.2	14.6	584
570	10	45.5	44.8	37.4	.375	34.5	920.0	65.4	.122	.253	.667	43.8	59.2	15.4	609
550	15	44.7	44.0	36.5	.3796	33.6	884.9	64.2	.119	.26	.685	44.0	59.2	15.2	585
530	20	44.6	43.9	35.8	.4074	32.6	800.2	65.6	.116	.291	.713	46.8	59.2	12.8	441
510	25	44.6	43.9	35.7	.412	32.5	788.9	65.0	.1135	.298	.725	47.2	59.2	12.0	400
490	30	44.6	43.9	35.5	.4212	32.1	762.1	64.6	.109	.3122	.74	47.8	58.4	10.6	340
470	40	44.6	43.9	35.4	.4251	32.0	751.3	64.2	.1078	.3173	.746	47.85	57.6	9.75	308
450	50	44.3	43.5	35.0	.4305	31.6	734.0	64.0	.1048	.3257	.755	48.4	56.8	8.4	260
430	60	43.5	42.6	34.0	.4397	30.6	695.8	63.6	.102	.3377	.768	48.9	56.1	7.2	213
410	120	43.3	42.4	35.7	.444	30.3	681.7	60.6	.0975	.3465	.78	47.3	55.4	8.1	233
390	240	43.1	42.2	33.4	.449	29.9	665.1	59.8	.096	.353	.786	47.0	54.6	7.6	213
370	360	42.9	42.0	33.1	.4536	29.6	652.5	58.6	.0931	.3605	.795	46.6	53.8	7.2	200
350	480	42.7	41.7	32.8	.4582	29.2	637.2	57.4	.0904	.3678	.803	46.2	53.0	6.8	185
330	600	42.4	41.5	32.5	.4582	28.9	630.6	56.6	.0874	.3708	.81	45.8	52.3	6.5	175



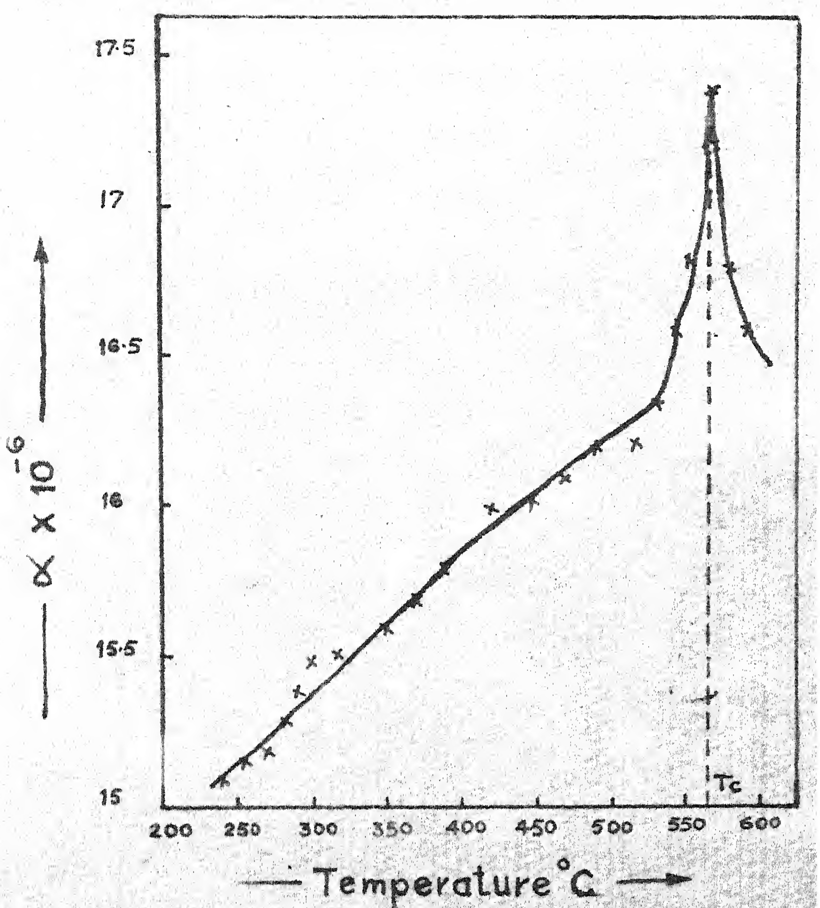
Resistivity Parameters Vs. Quench Temp. for 27·7 at.% Al Alloy.

Fig. 7



Observed and Computed Resistance Vs. Temp.

Fig. 8.



Coefficient of Thermal Expansion
Vs.
Temperature for 27·7 at. % Al Alloy

Fig. 9

from column 5 and this is reported in columns 10. The F'/F ratio is given in column 11. From the data in columns 8 and 11, F' $(P_A + P_T)$ has been calculated and is given in column 12. The experimentally observed resistance values at selected temperatures taken from Table III are given in Column 13. It may be noted that the temperature in column 1 corresponds to the measuring temperature and not the quench temperature when referring to the values in column 13. The resistance values ρT of column 13 are related to the resistivity parameters by equation (1.5). F'P_S is given by the difference in ρT values of columns 13 and 12 and this is reported in column 14. Column 15 gives P_S value calculated from the data in columns 14 and 10.

In Figure 7 variation of P_A^{QT}, F^{QT}. P_A^{QT} and F^{QT} with equilibration temperature i.e. quench temperature is shown. Observed (curve 1) and estimated resistance values (curves 2 and 3) as a function of temperature are shown in Figure 8. As an insert in this figure the variation of F'P_S and P_S with temperature is shown. The coefficient of thermal expansion as a function of temperature is shown in Figure 9.

CHAPTER 5

DISCUSSION

In the plot of coefficient of thermal expansion vs. temperature (Figure 9) we observe a distinctive peak at 568°C. This corresponds to the structural transition temperature T_c. However, the value of T_c obtained in the present investigation is about 15-20°C higher than that obtained by Lawley and Cahn (Table II). The observed α values are comparable to those reported by McQueen and Kuczynski$^{(2)}$. The hump observed in α-T curve at T_c is similar to the humps observed in their plots for various Fe-Al alloys.

The variation of the resistivity parameters F^{QT} and P_A^{QT} with equilibration temperature for the alloy of this investigation (Figure 8) , in general, appears to be similar to that exhibited by 24.8 atomic percent aluminum alloy (Figure 3). The variation of F^{QT} and P_A^{QT} with QT is much smaller in 27.7 atomic percent Al alloy compared to the stoichiometric alloy; this becomes evident from a comparison of Figures 7 and 3. For 27.7 atomic percent Al alloy (Figure 7) F^{QT} shows a steep fall between 530-550°C. Also the conspicuous flattening of the F^{QT} and $F^{QT}.P_A^{QT}$ curves occur just above T_c in case of 24.8 atomic percent Al alloy while in the present case this is not so. In the present case F^{QT} curve flattens at about 550°C while $F^{QT}.P_A^{QT}$ curve flattens at 570°C. The steep increase in P_A^{QT} curve occurs from about 500°C in Figure 3 while it occurs from 530°C in Figure 7

The increase in the value of F as the atomic order builds up can be explained on the lines followed by Coles$^{(6)}$ for the case of Cu_3Au. The electron mobility is diminished as new Brillouin zones corresponding to the changing lattice order are created and as a result of this the Fermi level is brought closer to a plane of energy discontinuity. This decrease in electron mobility is indicated by increase in the factor F. The conclusion from the curves of Figure 7 is that the decrease of resistance of quenched alloys with increasing order takes place inspite of a decreased freedom of conduction electrons (high value of F implies low degree of freedom and vice versa) since this increase of F is compensated by decrease of P_A.

In Figure 3 for 24.8 atomic percent Al alloy as quenching temperature diminishes P_A appears to approach asymptotically a value distinctly above zero, implying that order never becomes perfect for this alloy. This was the conclusion from X-ray data by Lawley et al$^{(21)}$ and also from the neutron diffraction data by Nathans et al$^{(22)}$. The variation of P_A with increasing order as shown in Figure 7 for the alloy of this investigation shows no such asymptotic behaviour. This is justified on the basis of Lawley's observation that most perfect order can be achieved around 28 atomic percent Al rather than at the stoichiometric composition of 25 atomic percent Al.

The effect of the interesting feature of θ_c being less than T_c for the alloy in this investigation can be seen in the curves of Figure 8. Curve 1 shows the observed resistance while curves 2 and 3 show the estimated and temperature-corrected values at various temperatures. Curve 2, Figure 8 shows a hump at about the Curie temperature (430°C). Similar hump, can be observed at θ_c temperature in curve 2, Figure 4 for the 24.8 atomic percent alloy. This indicates that the magnetic resistivity component is ~~being~~ coming into play at the Curie temperature, as expected. Another anomaly in resistance is noticeable in the vicinity of structural transition temperature, T_c(~ 550°C in 27.7 percent alloy). This may be compared with the resistance anomaly at T_c in 24.8 percent alloy (Figure 4, curve 2).

The high temperature correction to F results in curve 3, Figure 8. There is some uncertainity about the temperature correction applied to F and this curve is mainly meant to be useful for studying the variation of $F'P_S$ and P_S with temperature. The uncertainity in the temperature correction arises mainly in the arbitrarily taken ratio of F'/F as 2/3 at 590°C. The variation of P_S with temperature in Figure 8 indicates an increase in slope after the Curie temperature of 430°C due to the spin disorder resistivity.

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